



Separation of atrazine from water through thin-film composite membranes: influence of salts and surfactants

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ABSTRACT

The thin-film composite membrane is aptly named as thin polyamide layer on the asymmetric polysulfone membrane. These membranes have salt rejection abilities, and the order is $\text{NaCl} > \text{CaCl}_2$. Addition of NaCl increases (17.39% for 500 mg/L for Memb-II), whereas CaCl_2 decreases (5.94% for 500 mg/L for Memb-II) atrazine separation. Surfactant-mediated filtrations showed mixed results. Sodium lauryl sulfate (SLS) results better atrazine separation. SLS (200 mg/L) increases 29.72% separation for Memb-II. Contrary to SLS, Cetyl trimethyl ammonium bromide shows little negative influence (10.91%) and for Triton-X-100 (19.3%) it shows more deterioration effect for the same membrane, keeping the same concentration.

Keywords: Water; Atrazine; Membrane; Surfactant

1. Introduction

Coming face to face with ground realities that prevail in the developing world, the most important issue is “fresh water”. Population growth and rising per-capita consumption are causing increasing pressure on the availability of water resources. Water recycling is one of the approaches to meet our needs as well as fresh water reserve [1–4]. Many technological changes have been taken place in the agriculture world.

One of the side effects of these technological efforts is manifested in the pesticides polluted water and its adverse effect on human health [5–7]. Remediation of pesticides has been under serious study for the last few decades [8–11].

These classes of pollutants are general organic compounds having molecular weight of 200–400D. The striking fact that pesticides are the human creation to protect grains and vegetables from the pests, but due to ignorance of handling and uncertainty in climate, sometimes they are boomerang to human

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being. As water is one of the vehicles to transport, it is easily linked to the food chain. It is an appropriate time for scientists and technologists especially in developing countries, where water purification has never been the chosen form of escapism.

Since inception, people have taken different steps (viz. activated carbon filtration and ozone/UV treatment) in the direction of remediation of pesticides from water [12–18]. Assessments of the operating experience and design show that techniques have limitations (viz. rapid saturation of carbon filters, handling ozone is problematic as it is toxic, irritant to the skin, eyes, respiratory tract, and mucous membrane). Moreover, ozone and UV treatment results some residue in water. Since most attention usually gets diverted to the membrane filtration technique, as it is environment-friendly, low-cost energy consuming, and simple operating one [19–22].

It is potentially interesting for water processing, in particular, in the treatment or recycling of polluted water. No additives are required especially to proceed the separation and thus it is the clean one. Moreover, it has the potential to remove salts, color from water. Several studies have been carried out with nanofiltration membranes. For example, Ahmed et al. [23,24] examined four commercial nanofiltration membranes, NF90, NF200, NF270, and DK, to retain atrazine and dimethoate in aqueous solution. NF90 showed the highest rejection percentages (>90%) of all the membranes tested. Besides they found that NF90 membrane was more resistant to pH changes. Two of these membranes, NF200 and DK have also been tested [25] to remove pesticide residues, including atrazine, in water. High atrazine rejection percentages (between 80 and 90%) were obtained with both membranes.

In the present work, it is focused on atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine], the photosynthesis inhibiting triazinic herbicide. There are possibilities of water contamination with atrazine, as it is of high persistence in the environment, especially where cereals, sugar beets, white bean, onions, tomatoes, and turnips are cultivated. It has been reported [26] that almost 75% surface and 40% ground water are contaminated with atrazine in US. It has been implicated as potential endocrine disrupt compound in humans [27]. As the chemistry of commercial membranes is undisclosed, our target is to prepare membranes in laboratory scale. In this aspect, two thin-film composite (TFC) membranes are chosen based on different separation performance behavior in terms of salt rejection and markers (glucose and sucrose). These two membranes are used to study separation performances of synthetically prepared atrazine polluted water.

Membrane separation combined with surfactants has drawn attention in recent years. The versatility of surfactants arises because of the presence of both hydrophilic and hydrophobic moieties in the same molecule. This also indicates that membrane's performance is seen through the associative tendency with hydrophobic solutes. This work is of good importance for the simple reason so that the energy intensive process can be attractive. In the present context, three man-made surfactants viz. sodium lauryl sulfate (SLS) (anionic), cetyl trimethyl ammonium bromide (CTAB) (cationic), and Triton-X-100 (non-ionic) are chosen. The objective of study is to establish effects of salts and surfactants in the remediation of atrazine from water through low pressure TFC membranes.

2. Materials and methods

2.1. Materials

Atrazine (Sigma Chemicals, USA), Polysulfone (Udel, P-3500, Solvey Advanced Polymers, USA), m-phenylene diamine (MPD) (Lancaster, USA), and trimesoyl chloride (TMC) (Lancaster, USA) were prime chemicals for the experiment. Non-Woven polyester fabric (Filtration Sciences Corp., USA), N, N, Dimethyl formamide (Merck, India), and Sodium lauryl sulfate (SLS, sd fine Chemicals, India) were also used.

Glucose (Glaxo, India) and Sucrose (sd fine chemicals, India) were used as organic markers for the characterization of two membranes in terms of separation abilities. Methanol (sd fine chemicals, India) was used to prepare atrazine solution. Reverse osmosis treated water was used in the experiment.

Sodium chloride (Ranbaxy Chemicals, India) and Calcium chloride (sd fine chemicals, India) were used for salt rejection as well as to study their effects in atrazine separation of the membranes. Sodium lauryl sulphate (SLS [anionic]) (sd fine Chemicals, India), Cetyl trimethyl ammonium bromide (CTAB, cationic), (Sigma Chemicals, USA), and Triton-X-100 (neutral) (Alpha Chemika, India) were used as surfactants to study the effect in atrazine separation of the membranes.

2.2. Preparation of feed solution

An appropriate amount of methanol solution was taken to dissolve atrazine (1 mg/L). Five milliliters solution from the stock was taken in 2 L reverse osmosis treated water. Sodium and calcium chloride (100, 500 mg/L) were added into the atrazine feed solution to study the effect on membrane separation performance. Three surfactants SLS, CTAB, and Triton-X-100 in different concentrations (25, 50, 100, 200 mg/L)

were added to the solution to study the effects of atrazine separation.

2.3. Preparation of TFC membrane

Asymmetric polysulfone membranes were prepared from conventional wet-phase inversion technique. A homogeneous polysulfone solution (15% (w/w)) in N, N dimethyl formamide was prepared by slow dissolution of polysulfone beads at 45–50°C by continuous stirring. The solution is kept at room temperature for 3 h to avoid air bubbles which can cause defects in polysulfone membrane. Thin film of polysulfone solution was casted over the non-woven polyester fabric (100 µm) by moving it over the guide roller using a proto-type casting machine. The polysulfone solution casted non-woven fabric was then immersed into the non-solvent gelation bath i.e. water at 26°C. This results the demixing of solvent (dimethyl formamide) and non-solvent (water) to phase out solid asymmetric polysulfone membrane, having thickness 127 µm.

Polyamide composite membranes having thickness 130 µm were prepared by interfacial polymerizing of MPD and TMC on the surface of prepared polysulfone membranes. The interfacial polymerization of MPD (2% w/v in water) and TMC (0.1% w/v in hexane) was done on polysulfone membranes surface (16 × 13 cm) fitted on glass tray, kept for 3 min at room temperature and cured at different temperature. The preparation conditions are in ensemble. (Table 1).

2.4. Analytical method for atrazine/glucose/sucrose

The concentrations of atrazine and other organics were analyzed with high-performance liquid chromatography (Water Alliance model coupled with waters-2996) (reverse phase) under the following conditions: Column: Phenomenex Luna C18 (2) (Supelco) 250 mm × 4.2 mm × 5 µm, mobile phase acetonitrile / water (Rankem) (80:20) (containing 0.3% acetic acid), flow = 1.0 ml/min, 2996 PDA detector (λ_{\max} = 228 nm), temperature 30°C, injection volume: 50 µL. The reverse phase mode actually based on polarity difference (i.e. column is non-polar and mobile phase is polar). HPLC-Waters

2414 RI detector was used for carbohydrates (Glucose and Sucrose solution) analysis under the following conditions: Supelco Gel 610H column 300 mm × 7.8 mm × 9 µm, flow 0.5 ml/min, temperature 30°C, eluent 0.1% H₃PO₄ in water, and injection: 50 µL.

2.5. Techniques

Attenuated total reflection infrared spectroscopy (with a PerkinElmer Spectrum GX, Norwalk, CT with a resolution of ± 4 cm⁻¹ and an incident angle of 45°) of the surface layer of the membrane was performed to confirm the presence of polyamide functionality on TFC membrane. The membranes were visually characterized by Scanning Electron Microscopy (Leo, 1430UP, Oxford Instruments, UK).

The contact angles of membranes (before as well as after passing through feed with surfactants) were measured by Tensiometer (DCAT 21 from Dataphysics, Germany). The parameters were—motor speed 0.2 mm/s, dipping length 5 mm. The contact angles were determined, using Eq. (1) i.e. energy balance approach to three phase equilibrium.

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (1)$$

where γ represents the surface tension for the particular interface. The symbols *s*, *l*, and *v* are designated for solid, liquid, and vapor, respectively.

2.6. Permeability studies

The permeability was measured with a laboratory made pressure cell by cross-flow filtration technique at room temperature. The schematic diagram was presented in our earlier experiment [28]. The cross-flow filtration technique (i.e. feed passing parallel to membrane) was used for testing the separation of organics through membrane. The flow rate of solution was 48 L h⁻¹ and effective membrane area was 0.00152 m². The permeability was monitored at 1.4 MPa. Permeate for the analysis was collected after 1 h.

The separation performance is determined from analysis using the following Eq. (2)

Table 1
Preparation conditions of TFC membranes

Membrane	Polysulfone in DMF	Reactants for interfacial polymerization	Curing temp. (°C) in TFC membrane preparation
Memb-I	15% (w/w)	m-phenylene diamine (2% w/v)	60–65
Memb-II		Trimesoyl chloride (0.1% w/v)	80–85

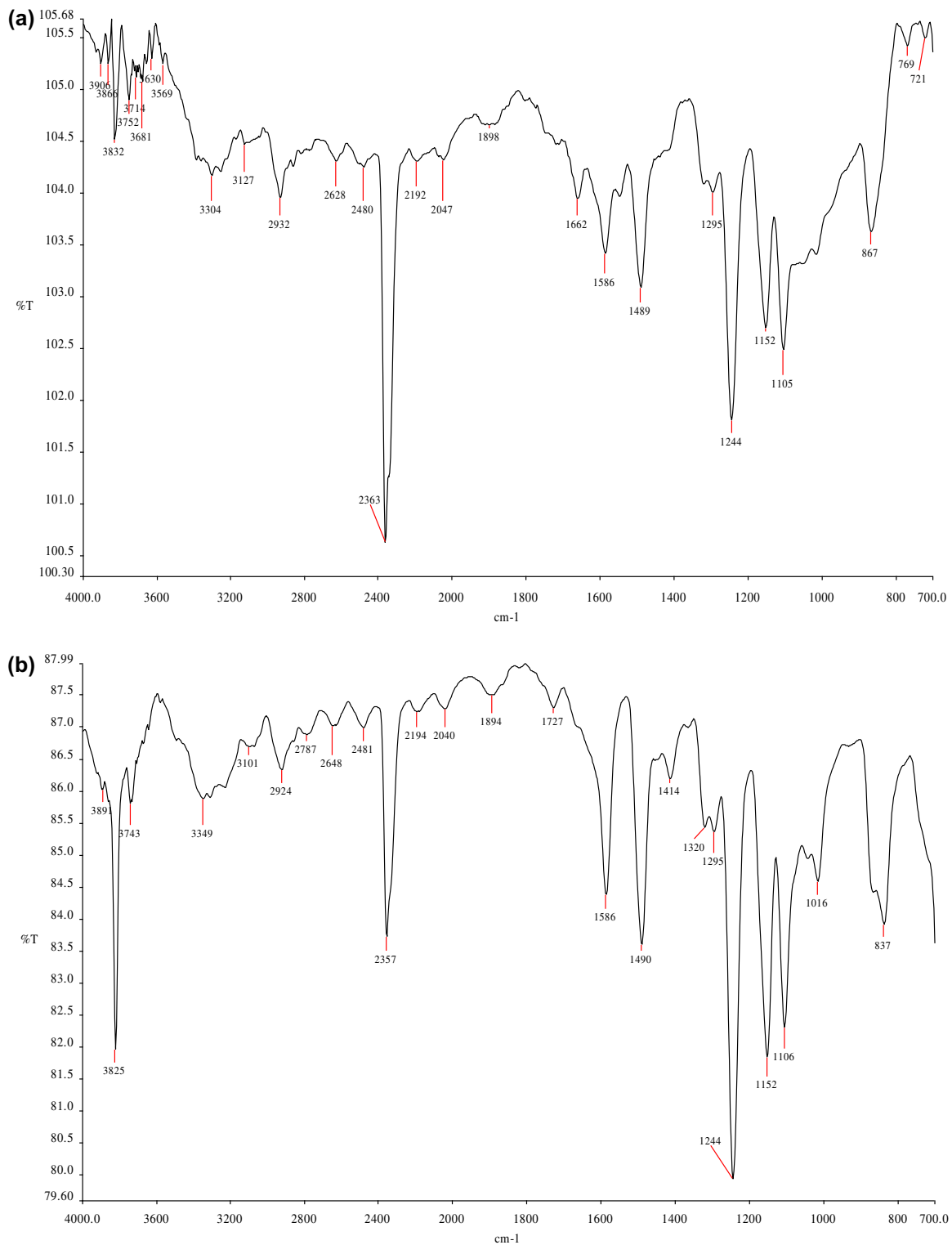


Fig. 1. FTIR spectra of (a) non-woven polyester fabric, (b) polysulfone, and (c) TFC membranes.

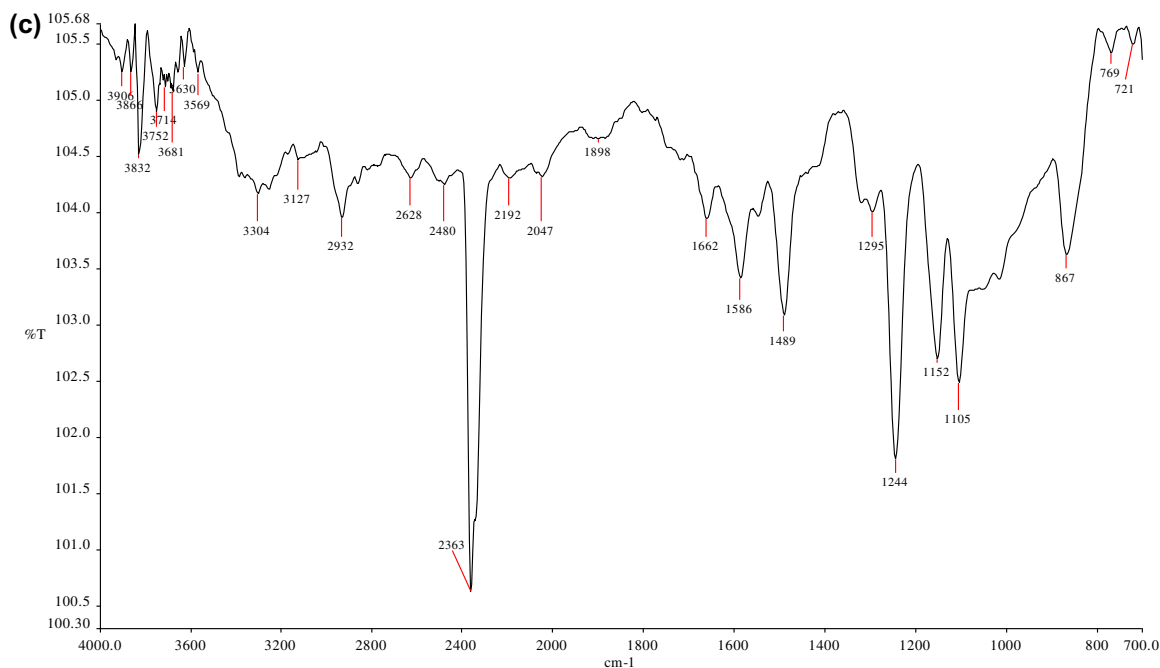


Fig. 1. (Continued).

$$R(\%) = \left(1 - \frac{c_p}{c_f}\right) \times 100 \quad (2)$$

where c_p and c_f are the concentrations of permeate and feed, respectively.

c_p and c_f are correlated with conductivity relationship for strong electrolytes and organics in water from HPLC. The flux is calculated by Eq. (3)

$$\text{volume flux} = \frac{l}{t \times A} \quad (3)$$

where l indicates the volume of permeate in liter, t in h and A is effective membrane area (m^2).

3. Results and discussions

3.1. Preparation of membranes

Membranes are prepared from the polymer (polysulfone), solvent (N,N dimethyl formamide) and non-solvent (water). Asymmetric trends have always picked up from wet-phase inversion technique. The diffusion exchange of solvent and non-solvent in the gelation bath (i.e. kitchen) is a growing trend of morphology of the membrane. Sodium lauryl sulfate is used in the gelation bath to control the uniformity of pores in the membrane. Dimethyl formamide solvent

for polysulfone is preferred because of its slow dissolution nature, so that it does not lead to fast and poorly controlled non-homogeneous deformation [29]. It is known for thin dense layer over the top and nodular structure at bottom of the thin dense layer [30]. The thin dense layer controls selectivity and other nodular part controls the permeation. The performance is total reflection of two structures.

In addition to that the cross-linked polyamide (made from MPD in water and trimesoyl chloride in hexane) over the top skinny polysulfone imparts rejuvenation to membrane property. The interfacial polymerization of MPD and trimesoyl chloride is the key reaction to form polyamide skin layer. Though it is termed interfacial, the reaction occurs in organic (hexane) phase as high partition co-efficient limits its availability in aqueous phase [31].

3.2. Physical characterization

Fig. 1 shows FTIR-ATR spectra of non-woven polyester fabric (a) and polysulfone membranes (b). The strong reflectance at $1,586\text{--}1,490\text{ cm}^{-1}$ is related to benzene ring stretching mode. The presence of sulfone group is easily be traced by bands at $1,152\text{ cm}^{-1}$. Asymmetric C–O stretching frequencies occur at $1,244$ and $1,016\text{ cm}^{-1}$. These observations are similar to earlier report depicted in literature [32–35]. In Fig. 1(c), the $1,662\text{ cm}^{-1}$ peak is observed because of

C=O stretching polyamide structure, C–N stretching at $1,586\text{ cm}^{-1}$, and amide (polyamide) peak at 769 cm^{-1} show the presence of polyamide (cross-linked) structure on TFC membrane. Two TFC membranes (Memb-I and Memb-II) show similar spectra. Thus, FTIR-ATR studies prove the polyamide structure on polysulfone membrane, reinforced on non-woven polyester fabric.

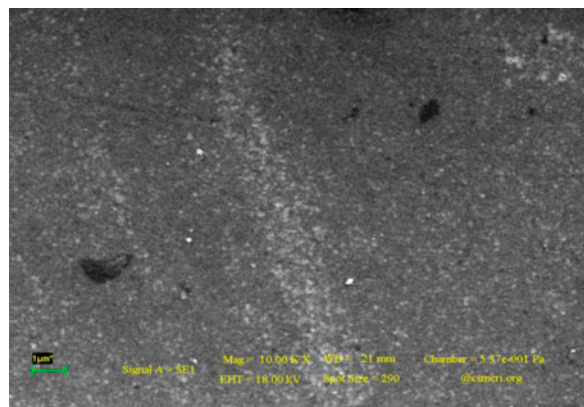
Fig. 2 shows the topographical scanning electron microscopic view of the PS (virgin) membrane and TFC membranes. Fig. 2(a) shows smooth structure of PS (virgin) membrane. TFC membranes (Fig. 2(b) and (c)) show distinct differences compared to surface morphology of virgin PS membrane. Memb-II shows the prominent features among two TFC membranes.

3.3. Characterization in terms of separation performances

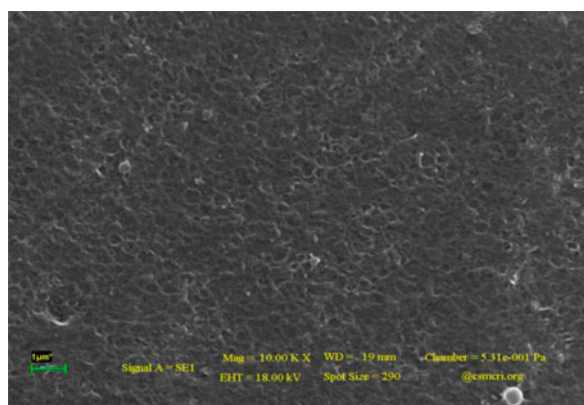
Thin polyamide layer on polysulfone is capable of reject both organic and inorganic electrolytes, making it convenient to characterize membranes. The membrane boasts of features such as size exclusion and charge-based separation. Molecular weight cut off i.e. separation ability $>90\%$ of that molecular weight) parameter though primarily related to molecular weight of the particular marker, it is better to consider molecular volume of experimented organics. In this study, glucose and sucrose are considered as organic markers. Table 2 shows physical parameters [36] as well as their separation performances of membranes. The retention of sucrose is higher than that of glucose, as expected from molecular volume of respective molecules.

The other aspect is reflected in their abilities of salt rejection (Table 2). The formation of $-\text{COOH}$ functionalities during cross-linking of diamine and trimesoyl chloride is the cause of development of negative charge on membrane surface [37]. The electrostatic interaction between membrane and ions in the solution has a major role to play for the charged membrane. The negatively charged co-ions (i.e. same charged ions with membrane charge) are repelled by the membrane whereas positively charged counter-ions (opposite to membrane charge) are in the vicinity of the membrane. Because of this concentration difference of ions, Donnan potential is generated between membrane and solution [38]. It results salt separation ability of membrane. It can also be explained by different theories (viz. preferential sorption, diffusion) [39].

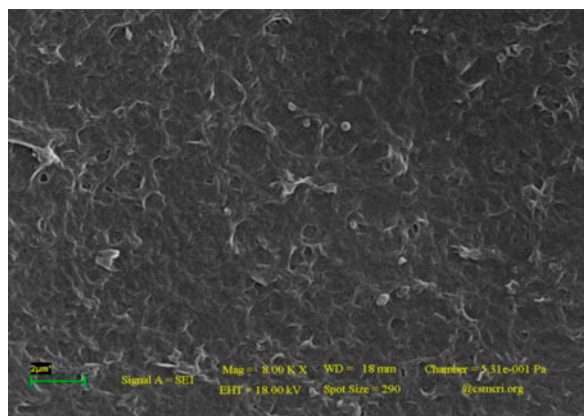
The salt rejection performance order (Memb-II $>$ Memb-I) can be explained by curing aspect. Actually, better curing stabilizes cross-linked polyamide on polysulfone and develops better functionalities. For negatively charged membrane, counter ions Ca^{2+} influence the potential more compared to Na^+ . Thus, the lower



(a)



(b)



(c)

Fig. 2. Scanning electron micrograph of (a) polysulfone (b) and (c) are two TFC membranes.

retention of CaCl_2 (counter ion (bivalent)—co-ion (monovalent)) than NaCl (counter ion (monovalent)—co-ion (monovalent)) is in accordance to Donnan Exclusion model and solution diffusion model [38,40,41] (Table 2). It is also supported by the corresponding volume flux (J_v).

Table 2

Separation performances of glucose, sucrose, and salts through membranes (Feed concentration for marker 500 mg/L and for salt: 2000 ppm), pressure 1.4 Mpa)

	Glucose (C ₆ H ₁₂ O ₆) (Mol. vol.: 203.7A ³) (Mol. wt.:180.16)	Sucrose (C ₁₂ H ₂₂ O ₁₁) (Mol. Vol.: 279 A ³) (Mol. Wt.: 342.30)	Sodium chloride	Calcium chloride
Memb-I	52.1	62.57	37.73	28.89
R (%)	14.7	11.3	9.8	5.8
Flux, LM ⁻² H ⁻¹				
Memb-II	70.09	84.84	79.55	62.89
R (%)	16.1	12.5	11	6.8
Flux, LM ⁻² H ⁻¹				

3.4. Separation performances of atrazine with the addition of salts

Atrazine separations, as synchronized to organic markers (glucose and sucrose) and salts, have been following the same trend. Chromatograms of the atrazine solution are presented in Fig. 3. Memb-II exhibits higher separation compared to Memb-I. (Fig. 4)

Fig. 4 also shows the variation of atrazine separation in presence of CaCl₂ and NaCl of two membranes (Memb-I and Memb-II). It shows diametrically opposite behavior in presence of two salts. When salt is added to atrazine solution, two major possibilities may arise: (1) pore swelling and (2) salting out [42]. The swelling of pores results due to repulsion forces between the counter ions in the electrical double layer at the pore walls. The salting out i.e. thinning of hydration layer around atrazine molecules decreases the effective size of the solutes [43]. It results deterioration in separation, as observed for the addition of CaCl₂.

Comparing between the two salts CaCl₂ and NaCl, it is seen (in Hoffmeister series) that Ca²⁺ shows strong hydration with respect to Na⁺. Further support is from its hydration enthalpy value (i.e. the energy released when one mole of substance is dissolved in to solution). The hydration enthalpy of Ca²⁺ (–1,602 kJ/mole) is higher compared to Na⁺ (–416 kJ/mole) [44]. They are always negative as attractive bonds (dative, ion-dipole). The greater hydration energy results in more strongly held water molecules in the hydration sphere of Ca²⁺. Thus, it inhibits development of strong interactions between polar head of atrazine (vector more towards chlorine functionality) and Ca²⁺. Compared with Na⁺ layered TFC membranes, the larger interlayer distance of Ca²⁺ layered TFC membrane and strong hydration of Ca²⁺ impede the direct contact of atrazine. Thus, there is the feasibility of better permeation through membrane and consequently less separation in presence of Ca²⁺. The trend is similar for both membranes (Memb-I and Memb-II). They suffer loss in separation 6.74 and

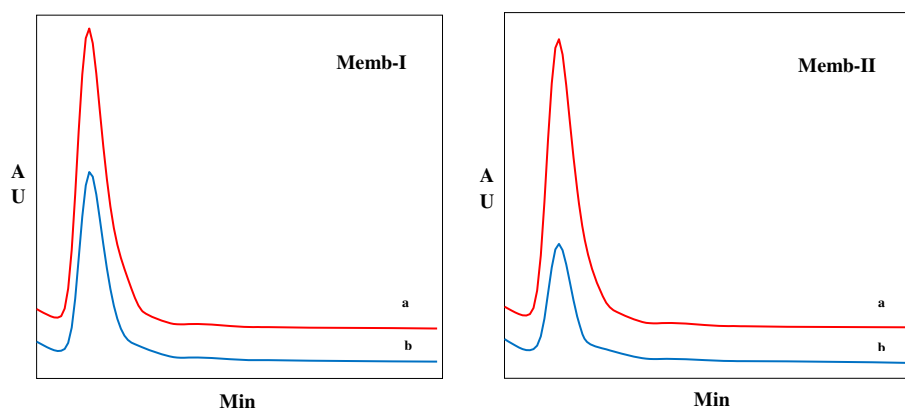


Fig. 3. HPLC Chromatograms of atrazine solution (a) feed and (b) permeate for two TFC membranes.

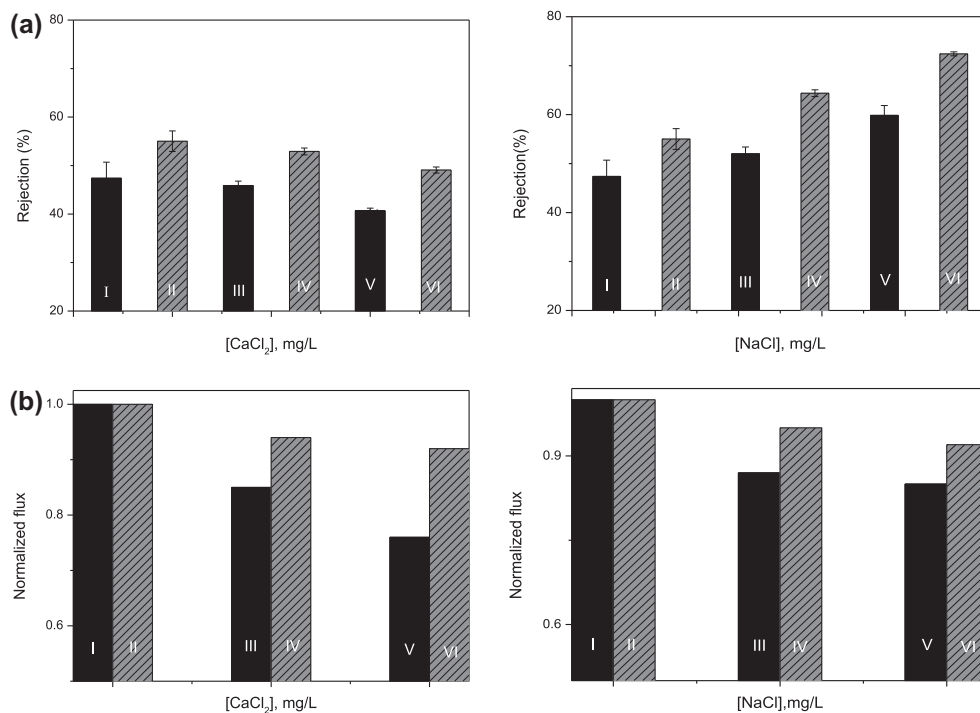


Fig. 4. Variation of separation performances (rejection (a) and flux, normalized (b)) of atrazine (1 mg/L) with different salt concentrations (I and II for atrazine only (Memb-I and II respectively), III and IV. Atrazine + CaCl₂/NaCl 100 mg/L (Memb-I and II respectively), V and VI. Atrazine + CaCl₂/NaCl, 500 mg/L (Memb-I and II respectively), pressure 1.4 MPa).

5.94%, respectively, with the addition of CaCl₂ (500 mg/L). In case of NaCl, the situation is opposite may be because of the weak hydrated Na⁺ ions, considering similar swelling. In this case, the effective size of atrazine with the hydrated ions is more. Thus, the addition of NaCl gains in separation 12.46 and 17.39%, respectively, for Memb-I and II in the same concentration (500 mg/L).

The normalized flux variation of two membranes is also displayed in Fig. 4(b). It shows decreasing trend for both membranes. The flux reduction may be due to increasing osmotic pressure, by addition of salt. The increasing water viscosity in pores [45] and bulk viscosity [46] due to the presence of salt ions could result in low flux.

3.5. Separation of atrazine with the addition of surfactants

Aqueous surfactants have two components i.e. hydrophilic and hydrophobic. The tail group is generally hydrophobic chain. Head groups are classified by their nature (anionic, cationic and non-ionic). "Adsolubilization" phenomena are observed as surfactants exist preferentially at interfaces. It is because of the association of hydrophobic moieties as they have poor

interaction of moieties with the aqueous media [47]. To explore the performances of membranes for atrazine separation, three different man-made surfactants (viz. sodium dodecyl sulphate (*anionic, critical micelle concentration (cmc): 0.0082 M*), CTAB (*cationic cmc: 0.92 M*), Tritone-X-100 (*non-ionic, cmc: 0.22 mM*)) are added. Critical micelle concentration (cmc) is defined as the particular concentration of surfactants which micelles start to grow spontaneously and it is one of the most important physical parameters of the surfactants. Here, the study is carried out well before cmc values of surfactants, considering low pressure driven TFC membrane. The initiative threw up mixed results.

Addition of SLS exerts significant influence in atrazine separation. The separation performance is depicted in Fig. 5. As it is known, SLS has one amphiphilic hydrophobic head and natural tendency to reorient them to be isolated from aqueous phase and adsorption into the organics (i.e. atrazine) and the hydrophilic part is in aqueous medium [21,36]. Thus, the association between atrazine and SLS leads to increase in the effective molecular size and improvement in separation results considering the sieving mechanism.

Fig. 5(a) shows improvement in separation performance with the increase in SLS concentrations. The

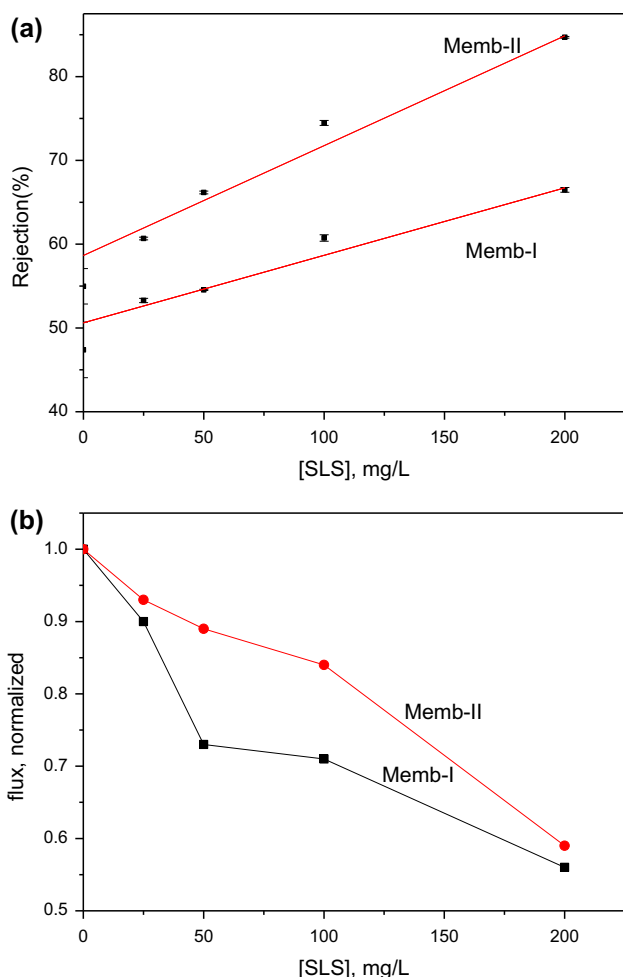


Fig. 5. Variation of separation performances (rejection (a) and flux, normalized (b)) of atrazine (1 mg/L) with different SLS concentrations, pressure 1.4 MPa.

absorption of SLS on membrane is proved by the decrease in contact angle (maximum decrement $\sim 4^\circ$) as well as flux reduction (Fig. 5(b)). The flux data are normalized compared to flux of atrazine only. The flux variation of two membranes is also displayed in Fig. 5. Apart from these, hydrophobicity factor ($\log P$, *n*-octanol/water partition co-efficient) of atrazine also influences separation. The high $\log P$ value of atrazine (2.61) [11,48] justifies the tendency to away from hydrophilic SLS absorbed surface.

Thus, the association with atrazine, absorption on membrane as well as hydrophobicity factor act as synergy in separation. Comparing slopes (Memb-I and Memb-II: 0.08 and 0.13, respectively) of two fitted linear curve, it shows that Memb-II (Adj. R^2 0.987) have more increasing trend in separation compared to Memb-I (Adj. R^2 0.97). As flux reduction is reflected more in case of Memb-I, the availability of surfactants

are less to bind atrazine in the solution compared to Memb-II. It suggests that size factor is dominating one in case of SLS and atrazine.

On the contrary, separation performances of atrazine with the addition of CTAB (cationic surfactant) are not improved for two membranes. The performance results are displayed in Fig. 6. The presence of CTAB in water feed has more tendencies to attach with membrane more as the membrane inbuilt charge is slightly negative because of the presence of residual $-\text{COOH}$ functional group (as mentioned earlier). Thus, the hydrophilic part is attached to membrane surface and hydrophobic ones are in the direction of aqueous phase. The contact angle increases $\sim 2^\circ$ for membranes. The more flux reduction compared to SLS treated membrane is observed. The result is similar to earlier experiment where it is also supported by comparative water flux recovery ratio [49]. The preference of CTAB

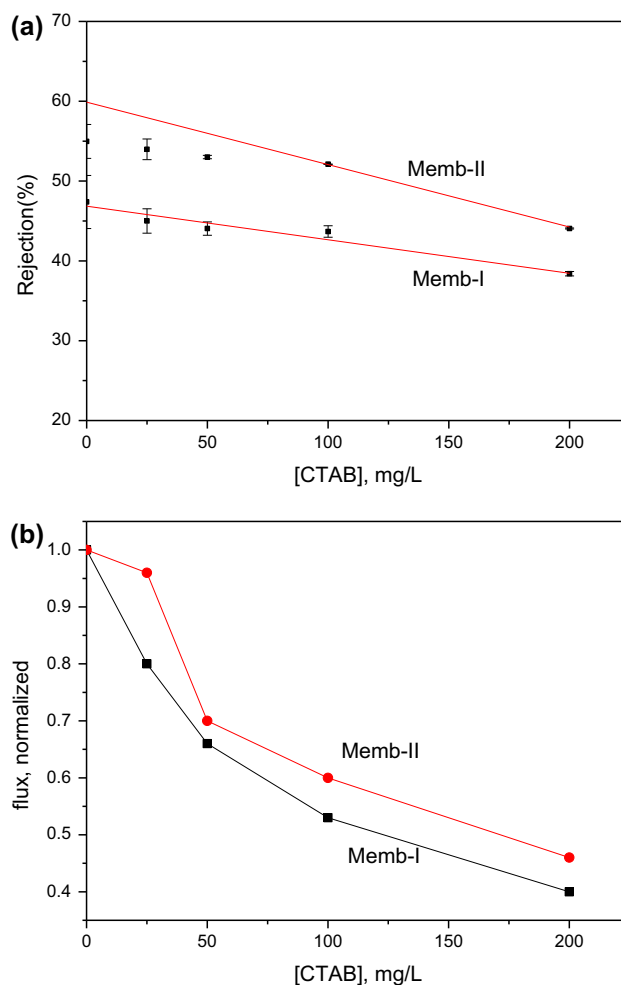


Fig. 6. Variation of separation performances (rejection (a) and flux, normalized (b)) of atrazine (1 mg/L) with different CTAB concentrations, pressure 1.4 MPa.

over SDS is also observed in negatively charged cell surface [50,51]. Though hydrophobicity of CTAB is relatively more compared to SDS due to higher chain length [52], the interaction with membrane effectively results poor concentration in aqueous phase and interaction with atrazine is comparatively less [53]. As membrane becomes hydrophobic, atrazine (hydrophobic) also tends towards membrane and results better permeation. Considering the linear fitting of data points (Fig. 6(a)), Memb-II (Adj. R^2 0.975) (slope: -0.07) shows slightly higher decreasing trend in separation compared to Memb-I (Adj. R^2 0.957) (slope -0.04), as membrane-CTAB association and hydrophobicity factor play a negative role. The flux variation (in normalized form) of two membranes is also displayed in Fig. 6(b). The pattern is same for both cases. It also shows more solution flux reduction compared with atrazine–sodium dodecyl sulfate associated one as the association of CTAB is more with the membrane.

In case of Triton-X-100, surfactant having hydrophilic polyethylene oxide ($-\text{CH}_2-\text{CH}_2-\text{O}-$) chain and aromatic hydrocarbon or hydrophobic group is non-ionic in nature. The interactions between functional groups ($-\text{COOH}$) on membrane surface and surfactant polar heads, probably inducing dipolar attraction as well as H-bonding are more than hydrophobic attraction between membrane and surfactant [50]. The hydrophilic part is rather added to hydrophilic membrane surface and hydrophobic part is open. Thus, contact angle is somewhat increased ($\sim 2^\circ$) for the particular membrane because of hydrophobicity. Atrazine being hydrophobic flows towards the membrane and thus permeation is easier compared to other. Because of favorable association with membranes, Triton-X-100 presence is less in the solution and thus the association with atrazine is less. The similar observation was established by Feria-Reyes et al. [54]. The separation performances of atrazine with the addition of Triton-X-100 (non-ionic surfactant) are displayed in Fig. 7. It shows that with the addition of Triton-X-100, rather than improving separation performances, it is hampered. Thus, membrane-Triton-X-100 association and hydrophobicity play the dominating negative role in separation performances of membrane here also. Fig. 7(a) shows that with increasing concentration of surfactant, separation follows decreasing trend and similar to both membranes (Memb-I and Memb-II). Considering linearity of the slopes of two fitted lines is -0.099 and -0.094 for Memb-I (Adj. R^2 : 0.975) and Memb-II (Adj. R^2 : 0.977), respectively. It also shows that there is not much difference in particular range of nature of membranes.

The flux (normalized) variation is displayed in Fig. 7(b). It shows with the addition of 25 mg/L

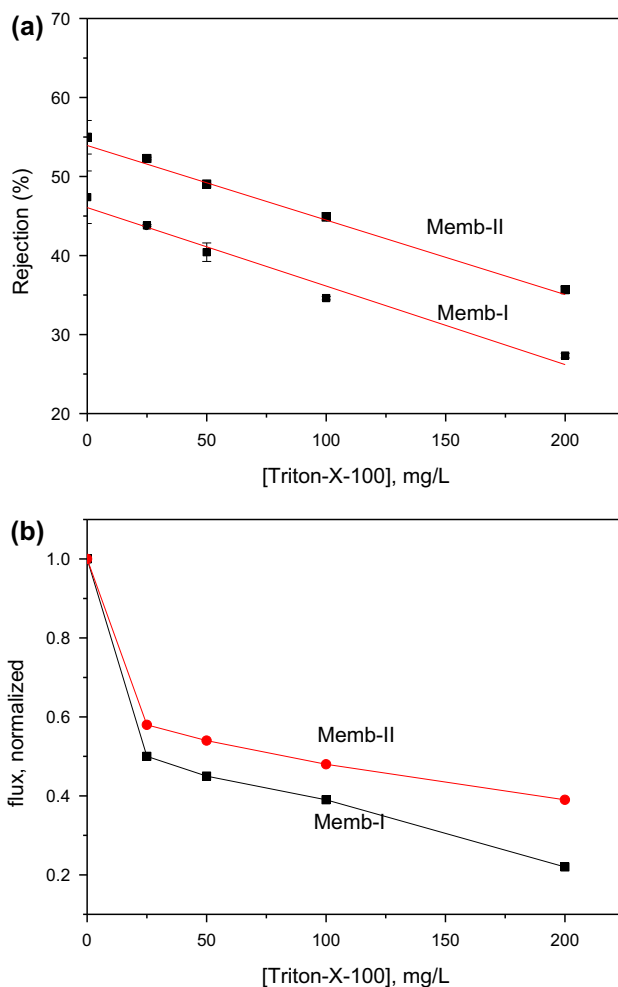


Fig. 7. Variation of separation performances (rejection (a) and flux, normalized (b)) of atrazine (1 mg/L) with different Triton-X-100 concentrations, pressure 1.4 MPa.

Triton-X-100, there is drastically change in flux (50% and 42% reduction for Memb-I and Memb-II), afterwards steady decrease pattern. Similar observation is also reported in case of mineral rejection properties as well as flux reduction [55]. The comparatively more flux reduction of membranes is observed with respect to membranes dealing with other surfactants (SLS and CTAB).

4. Conclusions

Membrane down the ages has led us to use TFC membranes. The signage of polyamide through interfacial polymerization of MPD and TMC on the asymmetric polysulfone membranes imparts the salt rejection property in it. The salt rejection follows the order: $\text{NaCl} > \text{CaCl}_2$. Low pressure driven membranes

having low salt rejection properties are chosen for the atrazine (herbicide) removal. The study leads to the following conclusions

- (1) The atrazine separation is in same trend with salt rejection as well as organic markers (glucose and sucrose) for the two TFC membranes.
- (2) Addition of NaCl results better atrazine separation (17.39% for 500 mg/L for Memb-II), whereas for CaCl₂ separation shows the reverse trend i.e. decreases (5.94% for 500 mg/L for Memb-II).
- (3) With the addition of SLS (anionic surfactant), atrazine separation has increased for both the membranes. It increases 29.72% for the addition of 200 mg/L SLS in case of Memb-II.
- (4) With the addition of CTAB (cationic surfactant), separation shows little deterioration (10.91% for 200 mg/L) for Memb-II.
- (5) In presence of Triton-X-100 (neutral surfactant) separation results more deterioration (19.3% for 200 mg/L) for Memb-II.

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